

# Selected ion flow tube study of the gas-phase reactions of $\text{CF}^+$ , $\text{CF}_2^+$ , $\text{CF}_3^+$ , and $\text{C}_2\text{F}_4^+$ with $\text{C}_2\text{H}_4$ , $\text{C}_2\text{H}_3\text{F}$ , $\text{CH}_2\text{F}_2$ , and $\text{C}_2\text{HF}_3$

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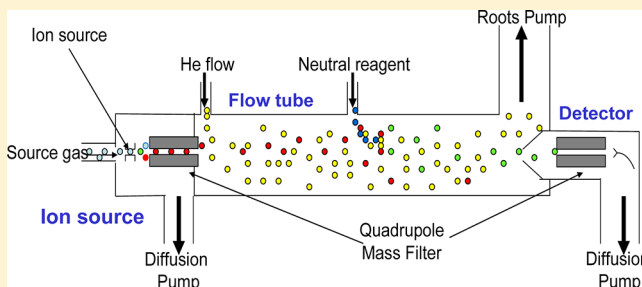
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Selected Ion Flow Tube Study of the Gas-Phase Reactions of  $\text{CF}^+$ ,  $\text{CF}_2^+$ ,  $\text{CF}_3^+$ , and  $\text{C}_2\text{F}_4^+$  with  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_3\text{F}$ ,  $\text{CH}_2\text{CF}_2$ , and  $\text{C}_2\text{HF}_3$ Matthew J. Simpson<sup>#</sup> and Richard P. Tuckett\*

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**ABSTRACT:** We study how the degree of fluorine substitution for hydrogen atoms in ethene affects its reactivity in the gas phase. The reactions of a series of small fluorocarbon cations ( $\text{CF}^+$ ,  $\text{CF}_2^+$ ,  $\text{CF}_3^+$ , and  $\text{C}_2\text{F}_4^+$ ) with ethene ( $\text{C}_2\text{H}_4$ ), monofluoroethene ( $\text{C}_2\text{H}_3\text{F}$ ), 1,1-difluoroethene ( $\text{CH}_2\text{CF}_2$ ), and trifluoroethene ( $\text{C}_2\text{HF}_3$ ) have been studied in a selected ion flow tube. Rate coefficients and product cations with their branching ratios were determined at 298 K. Because the recombination energy of  $\text{CF}_2^+$  exceeds the ionization energy of all four substituted ethenes, the reactions of this ion produce predominantly the products of nondissociative charge transfer.

With their lower recombination energies, charge transfer in the reactions of  $\text{CF}^+$ ,  $\text{CF}_3^+$ , and  $\text{C}_2\text{F}_4^+$  is always endothermic, so products can only be produced by reactions in which bonds form and break within a complex. The trends observed in the results of the reactions of  $\text{CF}^+$  and  $\text{CF}_3^+$  may partially be explained by the changing value of the dipole moment of the three fluoroethenes, where the cation preferentially attacks the more nucleophilic part of the molecule. Reactions of  $\text{CF}_3^+$  and  $\text{C}_2\text{F}_4^+$  are significantly slower than those of  $\text{CF}^+$  and  $\text{CF}_2^+$ , with adducts being formed with the former cations. The reactions of  $\text{C}_2\text{F}_4^+$  with the four neutral titled molecules are complex, giving a range of products. All can be characterized by a common first step in the mechanism in which a four-carbon chain intermediate is formed. Thereafter, arrow-pushing mechanisms as used by organic chemists can explain a number of the different products. Using the stationary electron convention, an upper limit for  $\Delta_f H^\circ_{298}(\text{C}_3\text{F}_2\text{H}_3^+)$ , with structure  $\text{CF}_2=\text{CH}-\text{CH}_2^+$  of  $628 \text{ kJ mol}^{-1}$  and a lower limit for  $\Delta_f H^\circ_{298}(\text{C}_2\text{F}_2\text{H}^+)$ , with structure  $\text{CF}_2=\text{CH}^+$  of  $845 \text{ kJ mol}^{-1}$  are determined.



## 1. INTRODUCTION

One consequence of the 1987 Montreal Protocol and its many later amendments has been the significant reduction over the last two decades in the use and production of ozone-depleting substances. These chemicals include chlorofluorocarbons (CFCs) and halons, commonly used in applications such as fire protection, refrigeration and aerosols. Many hydrofluorocarbons (HFCs) are considered to be less environmentally unfriendly alternatives to CFCs. This study investigates the effects on reactivity of a series of fluorinated ethenes  $\text{C}_2\text{H}_x\text{F}_{4-x}$  ( $x = 4, 3, 2, 1$ ) as the degree of fluorine substitution for hydrogen atoms in ethene increases. Reactivity is studied by determining the kinetics and products of reactions with small gas-phase cations. This work extends earlier similar studies by us of a series of chloroethenes, including the three isomers of dichloroethene.<sup>1,2</sup> The present study focuses on the reactions of ethene, monofluoroethene, 1,1-difluoroethene and trifluoroethene with the cations  $\text{CF}^+$ ,  $\text{CF}_2^+$ ,  $\text{CF}_3^+$ , and  $\text{C}_2\text{F}_4^+$  using a selected ion flow tube (SIFT). This study is not quite as extensive as for the chlorinated ethenes because the two 1,2-difluoroethene isomers of  $\text{C}_2\text{H}_2\text{F}_2$ , each thermodynamically less stable than the 1,1 isomer by ca.  $50 \text{ kJ mol}^{-1}$ , have not been investigated.

The results are compared with previous work, where available, on the reactions of  $\text{CF}_n^+$  ( $n = 1-3$ ) and  $\text{C}_2\text{F}_4^+$  ions with tetrafluoroethene and the chlorinated ethenes. This is the

first SIFT study on the reactions of these four cations with  $\text{C}_2\text{H}_3\text{F}$ , 1,1- $\text{CH}_2\text{CF}_2$ , and  $\text{C}_2\text{HF}_3$ . Using a variety of different techniques, the reactions of small fluorine-containing molecular cations with the related molecules  $\text{C}_2\text{H}_4$ , 1,2-difluoroethene, and  $\text{C}_2\text{F}_4$  have been investigated by several groups.<sup>3-12</sup> The work by Morris et al.,<sup>8,9</sup> who also used a selected ion flow tube, is particularly relevant. The reaction of  $\text{CF}_3^+$  with  $\text{C}_2\text{H}_4$  has been investigated by SIFT mass spectrometry<sup>10</sup> and with an ion beam apparatus.<sup>11</sup> The reactions of small molecular cations with the full series of fluorinated ethenes  $\text{C}_2\text{H}_x\text{F}_{4-x}$  ( $x = 0-4$ ) have also been studied using ion cyclotron resonance mass spectrometry (ICR-MS) by Bowers et al.<sup>3-7</sup>

The adiabatic ionization energies (IE) of  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_3\text{F}$ ,  $\text{CH}_2\text{CF}_2$ , and  $\text{C}_2\text{HF}_3$  are 10.51, 10.37, 10.30, and 10.14 eV, respectively.<sup>13-15</sup> Comparisons of these values with the recombination energy (RE) of the reagent ion (equal in magnitude to the adiabatic IE of the corresponding neutral) determines if charge transfer is energetically possible.<sup>16</sup> The RE values for  $\text{CF}^+$ ,  $\text{CF}_2^+$ ,  $\text{CF}_3^+$ , and  $\text{C}_2\text{F}_4^+$  are 9.11,<sup>17</sup> 11.36,<sup>18</sup> 9.09,<sup>19,20</sup> and 10.11 eV,<sup>15,21</sup> respectively, and so charge transfer is only exothermic for the reactions with  $\text{CF}_2^+$ .

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Table 1. Results for the Gas-Phase Reactions of  $\text{CF}^+$ ,  $\text{CF}_2^+$ , and  $\text{CF}_3^+$  with Ethene and the Fluorinated Ethenes

reaction <sup>a</sup>	$\Delta_f H^\circ_{298}$ <sup>b</sup> (kJ mol <sup>-1</sup> )	product branching ratio (%)	rate coefficient <sup>c</sup> (10 <sup>-9</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
$\text{CF}^+ + \text{C}_2\text{H}_4^d$	$\rightarrow \text{CH}_2\text{F}^+ + \text{C}_2\text{H}_2$	80	1.1 [1.3] 0.85
	$\rightarrow \text{C}_3\text{H}_3^+ + \text{HF}$	20	
$\text{CF}^+ + \text{C}_2\text{H}_3\text{F}$	$\rightarrow \text{C}_2\text{H}_3^+ + \text{CF}_2$	88	2.1 [2.0] 1.00
	$\rightarrow \text{CHF}_2^+ + \text{C}_2\text{H}_2$	12	
$\text{CF}^+ + \text{CH}_2\text{CF}_2$	$\rightarrow \text{CF}_3^+ + \text{C}_2\text{H}_2$	88	1.4 [1.9] 0.74
	$\rightarrow \text{C}_2\text{H}_2\text{F}^+ + \text{CF}_2$	7	
	$\rightarrow \text{CHF}_2^+ + \text{C}_2\text{HF}$	5	
$\text{CF}^+ + \text{C}_2\text{HF}_3$	$\rightarrow \text{CF}_3^+ + \text{C}_2\text{HF}$	100	1.0 [1.7] 0.59
$\text{CF}_2^+ + \text{C}_2\text{H}_4^e$	$\rightarrow \text{C}_3\text{H}_3\text{F}_2^+ + \text{H}^f$	55	1.1 [1.1] 1.00
	$\rightarrow \text{C}_2\text{H}_4^+ + \text{CF}_2$	45	
$\text{CF}_2^+ + \text{C}_2\text{H}_3\text{F}$	$\rightarrow \text{C}_2\text{H}_3\text{F}^+ + \text{CF}_2$	88	1.8 [1.8] 1.00
	$\rightarrow \text{C}_2\text{H}_3^+ + \text{CF}_3$	12	
	$\rightarrow \text{CH}_2\text{CF}_2^+ + \text{CF}_2$	100	
$\text{CF}_2^+ + \text{C}_2\text{HF}_3$	$\rightarrow \text{C}_2\text{HF}_3^+ + \text{CF}_2$	100	1.5 [1.5] 1.00
$\text{CF}_3^+ + \text{C}_2\text{H}_4^g$	$\rightarrow \text{C}_3\text{H}_3\text{F}_2^+ + \text{H}^h$	60	0.7 [1.1] 0.64
	$\rightarrow \text{C}_2\text{H}_3^+ + \text{CHF}_3$	40	
$\text{CF}_3^+ + \text{C}_2\text{H}_3\text{F}$	$\rightarrow \text{C}_2\text{H}_3^+ + \text{CF}_4$	75	1.3 [1.6] 0.81
	$\rightarrow \text{CHF}_2^+ + \text{CH}_2\text{CF}_2^j$	25	
	$\rightarrow \text{C}_2\text{H}_2\text{F}^+ + \text{CF}_4$	50	
$\text{CF}_3^+ + \text{CH}_2\text{CF}_2$	$\rightarrow \text{C}_3\text{H}_2\text{F}_5^+$ (adduct)	44	0.7 [1.5] 0.47, $p(\text{He}) = 0.5$ Torr
	$\rightarrow \text{C}_3\text{HF}_4^+ + \text{HF}^k$	6	
	$\rightarrow \text{C}_3\text{HF}_6^+$ (adduct)	100	
$\text{CF}_3^+ + \text{C}_2\text{HF}_3^l$	$\rightarrow \text{C}_3\text{HF}_6^+$ (adduct)		0.2 [1.3] 0.15, $p(\text{He}) = 0.5$ Torr

<sup>a</sup>The neutral products of these reactions are not detected in the experiment but are proposed as the most likely candidates. <sup>b</sup>The reaction enthalpy calculated from 298 K enthalpies of formation. <sup>c</sup>The experimentally determined rate coefficient,  $k_{\text{exp}}$ . In square brackets are the collisional values,  $k_c$ , and the rate efficiency is given as the ratio of  $k_{\text{exp}}$  to  $k_c$ . <sup>d</sup>Values used for  $\Delta_f H^\circ_{298}$  in kJ mol<sup>-1</sup>, are  $\text{CF}^+$  1122.3,<sup>20</sup>  $\text{C}_2\text{H}_4$  52.5,<sup>26</sup>  $\text{C}_2\text{H}_3\text{F}$  -140.1,<sup>32</sup> 1,1- $\text{C}_2\text{H}_2\text{F}_2$  -350.2,<sup>33</sup> and  $\text{C}_2\text{HF}_3$  -499.1.<sup>20</sup> Data for product species taken from refs 20, 26, and 27. <sup>e</sup>Value used for  $\Delta_f H^\circ_{298}(\text{CF}_2^+)$  is 897.1 kJ mol<sup>-1</sup>.<sup>20</sup> Data for product species taken from refs 20, 26, and 27. <sup>f</sup>Assuming this reaction is exothermic, we determine  $\Delta_f H^\circ_{298}(\text{C}_3\text{H}_3\text{F}_2^+) < 732$  kJ mol<sup>-1</sup>. Its structure is almost certainly  $\text{CF}_2=\text{CH}-\text{CH}_2^+$ . <sup>g</sup>Value used for  $\Delta_f H^\circ_{298}(\text{CF}_3^+)$  is 410.2 kJ mol<sup>-1</sup>.<sup>20</sup> Data for product species taken from refs 20, 26, and 27. <sup>h</sup>Assuming this reaction is exothermic, we determine  $\Delta_f H^\circ_{298}(\text{C}_3\text{H}_3\text{F}_2^+) < 735$  kJ mol<sup>-1</sup>. The cis and trans 1,2 isomers both give endothermic reaction enthalpies, and so we propose 1,1-difluoroethene is the neutral product species formed. <sup>i</sup>Assuming this reaction is exothermic, we determine  $\Delta_f H^\circ_{298}(\text{C}_3\text{HF}_4^+) < 333$  kJ mol<sup>-1</sup>. Its structure is almost certainly  $\text{CF}_2=\text{CH}-\text{CF}_2^+$ . <sup>j</sup>The absence of  $\text{C}_2\text{HF}_2^+$ , presumably with structure  $\text{CF}_2=\text{CH}^+$ , from this reaction by  $\text{F}^-$  abstraction suggests that  $\Delta_f H^\circ_{298}(\text{C}_2\text{HF}_2^+) > 845$  kJ mol<sup>-1</sup>.

## 2. EXPERIMENTAL SECTION

The reactions of the four titled fluorocarbon cations with  $\text{C}_2\text{H}_x\text{F}_{4-x}$  ( $x = 4, 3, 2, 1$ ) have been investigated at 298 K using a SIFT apparatus to determine rate coefficients, product ions, and their branching ratios (BRs), and whether the product ion is primary or secondary. The SIFT technique has been described in detail elsewhere.<sup>22–25</sup> Briefly, the four reagent cations were all generated from perfluoropropane,  $\text{C}_3\text{F}_8$ , in a high-pressure (ca. 10<sup>-4</sup> mbar) electron ionization source. A quadrupole mass filter was used to select the reagent ion before

injection into the flow tube, 1 m in length and 8 cm in diameter. The carrier gas was He at a pressure of ca. 0.5 Torr, flowing at a velocity of ca. 100 m s<sup>-1</sup>. Conditions inside the flow tube were thermalized at 298 K, and any excited ions produced in the source should be collisionally cooled by the buffer gas. At a known distance downstream in the flow tube the neutral reactant gas was injected. The reaction gas mixture was sampled at the end of the flow tube through a 1 mm orifice in a Faraday plate. Reactant and product ions were focused into a second

Table 2. Results for the Gas-Phase Reactions of  $\text{C}_2\text{F}_4^+$  with Ethene and the Fluorinated Ethenes

reaction <sup>a</sup>	$\Delta_r H^\circ_{298}$ (kJ mol <sup>-1</sup> ) <sup>b</sup>	product branching ratio (%)	rate coefficient <sup>c</sup> (10 <sup>-9</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
$\text{C}_2\text{F}_4^+ + \text{C}_2\text{H}_4^d \rightarrow \text{C}_2\text{H}_2\text{F}_2^+ + \text{C}_2\text{H}_2\text{F}_2^e$	-62 <sup>f</sup>	95	0.7 [1.0] 0.70
$\rightarrow \text{C}_3\text{H}_3\text{F}_2^+ + \text{CHF}_2^g$	?	5	
$\text{C}_2\text{F}_4^+ + \text{C}_2\text{H}_3\text{F} \rightarrow \text{C}_2\text{HF}_3^+ + \text{CH}_2\text{CF}_2^h$	-34	45	0.6 [1.5] 0.40,
$\rightarrow \text{C}_3\text{H}_3\text{F}_2^+ + \text{CF}_3^j$	?	40	$p(\text{He}) = 0.5$ Torr
$\rightarrow \text{C}_3\text{H}_2\text{F}_3^+ + \text{CHF}_2^k$	?	10	
$\rightarrow \text{CH}_2\text{CF}_2^+ + \text{C}_2\text{HF}_3$	-18	3	
$\rightarrow \text{C}_4\text{H}_3\text{F}_5^+$ (adduct)	?	2	
$\text{C}_2\text{F}_4^+ + \text{CH}_2\text{CF}_2 \rightarrow \text{C}_4\text{H}_2\text{F}_6^+$ (adduct)	?	60	0.7 [1.4] 0.50,
$\rightarrow \text{C}_3\text{H}_2\text{F}_3^+ + \text{CF}_3^l$	?	30	$p(\text{He}) = 0.5$ Torr
$\rightarrow \text{C}_3\text{HF}_4^+ + \text{CHF}_2^m$	?	10	
$\text{C}_2\text{F}_4^+ + \text{C}_2\text{HF}_3 \rightarrow \text{C}_2\text{HF}_3^+ + \text{C}_2\text{F}_4$	+3	72	0.2 [1.2] 0.17
$\rightarrow \text{C}_3\text{HF}_4^+ + \text{CF}_3^n$	?	28	

<sup>a</sup>The neutral products of these reactions are not detected in the experiment but are proposed as the most likely candidates. <sup>b</sup>The reaction enthalpy calculated from 298 K enthalpies of formation. Absence of a value indicates  $\Delta_r H^\circ$  for the product cation is not known. <sup>c</sup>The experimentally determined rate coefficient,  $k_{\text{exp}}$ . In square brackets are the collisional values,  $k_c$ , and the rate efficiency is given as the ratio of  $k_{\text{exp}}$  to  $k_c$ . <sup>d</sup>Value used for  $\Delta_r H^\circ_{298}(\text{C}_2\text{F}_4^+)$  is 302.7 kJ mol<sup>-1</sup>. <sup>e</sup>Data for product species taken from refs 20, 26, and 27. <sup>f</sup>The isomeric forms of these two product species are not known; however, it is proposed that both the cation and neutral are the 1,1-isomers of difluoroethene. <sup>g</sup>The calculated  $\Delta_r H^\circ$  value if the two product species are both the 1,1- isomers. <sup>h</sup>Assuming this reaction is exothermic, we determine  $\Delta_r H^\circ_{298}(\text{C}_3\text{H}_3\text{F}_2^+) < 605$  kJ mol<sup>-1</sup>. Its structure is almost certainly  $\text{CF}_2=\text{CH}-\text{CH}_2^+$ . <sup>i</sup>Both cis and trans 1,2 isomers give endothermic reaction enthalpies, and so we propose 1,1-difluoroethene is the neutral product species formed. <sup>j</sup>Assuming this reaction is exothermic, we determine  $\Delta_r H^\circ_{298}(\text{C}_3\text{H}_3\text{F}_2^+) < 628$  kJ mol<sup>-1</sup>. <sup>k</sup>Assuming this reaction is exothermic, we determine  $\Delta_r H^\circ_{298}(\text{C}_3\text{H}_2\text{F}_3^+) < 412$  kJ mol<sup>-1</sup>. Its structure is probably  $\text{CF}_2=\text{CH}-\text{CHF}^+$ . <sup>l</sup>Assuming this reaction is exothermic, we determine  $\Delta_r H^\circ_{298}(\text{C}_3\text{H}_2\text{F}_3^+) < 438$  kJ mol<sup>-1</sup>. <sup>m</sup>Assuming this reaction is exothermic, we determine  $\Delta_r H^\circ_{298}(\text{C}_3\text{HF}_4^+) < 202$  kJ mol<sup>-1</sup>. Its structure is probably  $\text{CF}_2=\text{CH}-\text{CF}_2^+$ . <sup>n</sup>Assuming this reaction is exothermic, we determine  $\Delta_r H^\circ_{298}(\text{C}_3\text{HF}_4^+) < 418$  kJ mol<sup>-1</sup>.

quadrupole mass filter and detected by an off-axis channeltron electron multiplier.

The experimental rate coefficients,  $k_{\text{exp}}$ , were measured under pseudo-first-order conditions by recording the loss of reagent ion as a function of the concentration of neutral reagent. The measurement of the latter's absolute concentration has been described in Appendix II of ref 25. The experimental uncertainty in  $k_{\text{exp}}$  values was estimated to be  $\pm 20\%$ , and the apparatus is limited to measuring reactions with  $k_{\text{exp}} \geq \text{ca. } 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Product ion BRs were obtained by recording their signals as a function of the concentration of the neutral reagent. The ion signals were then extrapolated to zero concentration to give the BRs, which also allows identification of any secondary ion products. The error in the BRs were considered to be  $\pm 20\%$ , although this value will be greater for minor products when BRs are below 10%.

$\text{C}_2\text{H}_3\text{F}$  (98%) and  $\text{C}_2\text{HF}_3$  (97%) were purchased from Apollo Scientific,  $\text{C}_2\text{H}_4$  (99.5%) and  $\text{CH}_2\text{CF}_2$  (99+%) from Aldrich, and  $\text{C}_3\text{F}_8$  (99+%) from Fluorochem. All gases were used without further purification.

### 3. RESULTS AND DISCUSSION

A summary of the results for the reactions of  $\text{CF}_n^+$  ( $n = 1-3$ ) and  $\text{C}_2\text{F}_4^+$  with  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_3\text{F}$ ,  $\text{CH}_2\text{CF}_2$ , and  $\text{C}_2\text{HF}_3$  are presented in Tables 1 and 2. The results include the product cations, their BRs and the bimolecular reaction rate coefficient,  $k_{\text{exp}}$ . In addition, neutral products associated with the product cation are proposed, the corresponding reaction enthalpies

calculated, and collisional rate coefficients,  $k_c$ , are included. Reaction enthalpies ( $\Delta_r H^\circ_{298}$ ) were calculated using enthalpies of formation ( $\Delta_f H^\circ_{298}$ ) for the reactant and product species, these values usually being taken from standard sources.<sup>26,27</sup> New  $\Delta_r H^\circ_{298}$  values for the reactant species, shown in the footnotes to Tables 1 and 2, are taken from a study of the photodissociative ionization dynamics of fluorinated ethenes using imaging photoelectron photoion coincidence spectroscopy.<sup>20</sup> The  $k_c$  values were calculated using the modified average dipole orientation (MADO) model.<sup>28,29</sup> Comparison of  $k_{\text{exp}}$  and  $k_c$  values can indicate the efficiency of a reaction, yielding information regarding its dynamics. To calculate  $k_c$  values, the polarizability volume and dipole moment, if applicable, for the neutral reactant species must be known. The data are shown in Table 3, including that for  $\text{C}_2\text{F}_4$  because reactions of this molecule have been studied by others.<sup>4,9,11</sup>

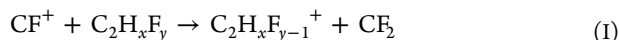
Table 3. Polarizability Volumes and Dipole Moments for Ethene and Four Fluorinated Ethenes

molecule	$\text{C}_2\text{H}_4$	$\text{C}_2\text{H}_3\text{F}$	$\text{CH}_2\text{CF}_2$	$\text{C}_2\text{HF}_3$	$\text{C}_2\text{F}_4$
$\alpha'/\text{\AA}^3$ <sup>a</sup>	4.25 <sup>c</sup>	3.99 <sup>d</sup>	5.01 <sup>c</sup>	4.16 <sup>d</sup>	4.35 <sup>d</sup>
$\mu_D/\text{D}$ <sup>b</sup>		1.47 <sup>c</sup>	1.39 <sup>c</sup>	1.32 <sup>c</sup>	

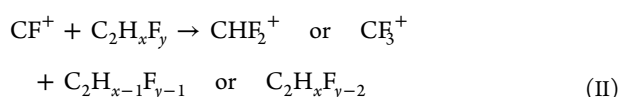
<sup>a</sup>Polarizability volume,  $\alpha'$ , given in  $\text{\AA}^3$  where  $1 \text{ \AA}^3 = 10^{-30} \text{ m}^3$ . <sup>b</sup>Dipole moment,  $\mu_D$ , in debyes (D) where  $1 \text{ D} = 3.336 \times 10^{-30} \text{ C m}$ . <sup>c</sup>Value from CRC Handbook of Chemistry and Physics.<sup>30</sup> <sup>d</sup>Value calculated using the method of Miller.<sup>31</sup>



**3.1. Reactions of  $\text{CF}^+$ .** Because the RE for  $\text{CF}^+$  is 9.11 eV,<sup>17</sup> charge transfer in reactions with all four titled ethenes is endothermic because the IE of the ethene always exceeds this value. Reactions can only occur through a chemical mechanism where bonds are formed and then broken in a reaction complex.<sup>16</sup> The results of Table 1 reveal that only two types of reaction are occurring. One is  $\text{F}^-$  transferred from the neutral species:



As fluorination increases, reaction I becomes *less* favorable; for  $\text{C}_2\text{H}_3\text{F}$  this reaction represents the major product channel (88%), for  $\text{CH}_2\text{CF}_2$  the BR falls to just 7%, and for  $\text{C}_2\text{HF}_3$  this reaction is not observed, presumably because it is endothermic. The second type of reaction involves either HF or  $\text{F}_2$  abstraction:



For  $\text{C}_2\text{H}_3\text{F}$  reaction II represents the minor product channel (12%), although it is more exothermic than the  $\text{F}^-$  abstraction channel. Now, as the degree of fluorination increases the BR associated with reaction II increases; the BR for  $\text{CH}_2\text{CF}_2$  is  $88 + 5 = 93\%$ , and for  $\text{C}_2\text{HF}_3$  it is 100%.

$\text{F}^-$  abstraction, reaction I, suggests that  $\text{CF}^+$  attacks the electron-rich fluorine in  $\text{C}_2\text{H}_x\text{F}_y$  rather than the  $\text{C}=\text{C}$  bond. Thus, it is probably the decrease in dipole moment as fluorination increases (Table 3) which is responsible for the trend in BRs noted; the larger the dipole moment, the more concentrated the electron density on an individual fluorine atom, and the more nucleophilic it becomes. For reaction II, there is no obvious mechanism to explain the observed products, but a tight transition state should be formed. It is also unclear if this mechanism involves breaking the  $\text{C}=\text{C}$  bond or not. The reaction of  $\text{CF}^+$  with  $\text{CH}_2\text{CF}_2$  produces two different outcomes from (II);  $\text{CF}_3^+ + \text{C}_2\text{H}_2$  and  $\text{CHF}_2^+ + \text{C}_2\text{HF}$ , with the BR of the former being much greater. We also note that  $\text{H}_2$  abstraction is not observed in either the reaction with  $\text{C}_2\text{H}_3\text{F}$  or  $\text{CH}_2\text{CF}_2$ . For  $\text{CH}_2\text{CF}_2$ ,  $\text{H}_2$  abstraction is endothermic by 71 kJ mol<sup>-1</sup>, but from  $\text{C}_2\text{H}_3\text{F}$  it is exothermic by 53 kJ mol<sup>-1</sup>. Although the competition between reactions I and II is not considered to be energetically driven, when considering reaction II alone,  $\text{F}_2$  abstraction is more exothermic than HF abstraction which is more exothermic than  $\text{H}_2$  abstraction. This suggests that energetics are being reflected in the BRs of the different products via (II).

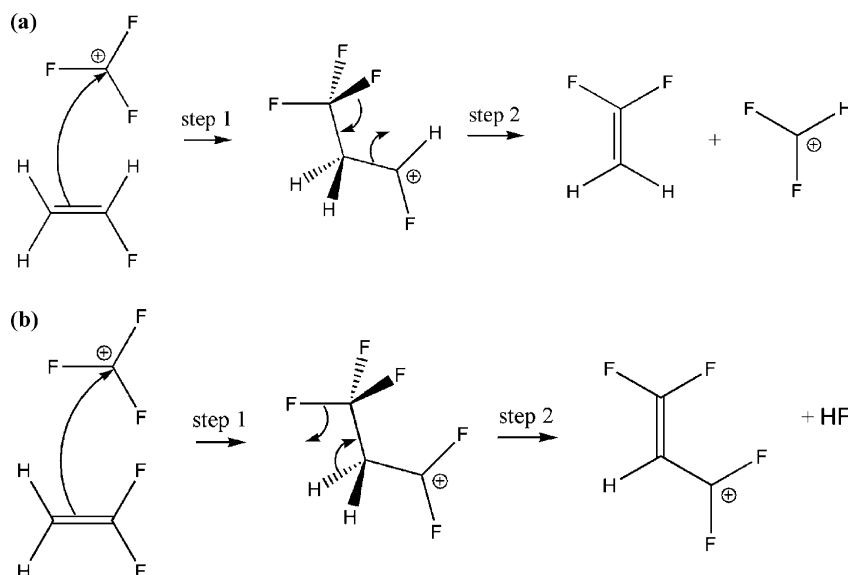
The reaction of  $\text{CF}^+$  with  $\text{C}_2\text{F}_4$  has been reported by Morris et al.,<sup>9</sup> and this reaction fits the trends observed from our study;  $\text{F}_2$  abstraction, reaction II, is observed as the major product ( $\text{CF}^+ + \text{C}_2\text{F}_4 \rightarrow \text{CF}_3^+ + \text{C}_2\text{F}_2$ ) and reaction I is not observed at all. However, the reaction with  $\text{C}_2\text{F}_4$  also produces the minor products  $\text{C}_3\text{F}_5^+$  and  $\text{C}_2\text{F}_4^+$  by association and charge transfer, respectively. The adiabatic IE of  $\text{C}_2\text{F}_4$  is 10.11 eV,<sup>18,21</sup> and so charge transfer to  $\text{CF}^+$  ( $\nu = 0$ ) is endothermic. This observation of  $\text{C}_2\text{F}_4^+$  product by Morris et al. is attributed to the reaction with electronically- or vibrationally excited  $\text{CF}^+$  (produced from electron impact ionization of  $\text{CF}_3\text{Br}$ ). In our experiments  $\text{CF}^+$  ions are produced by electron impact ionization from a different precursor,  $\text{C}_3\text{F}_8$ . Charge-transfer products from the reaction of  $\text{CF}^+$  with  $\text{C}_2\text{H}_3\text{F}$ ,  $\text{CH}_2\text{CF}_2$ , and  $\text{C}_2\text{HF}_3$  have not been observed. The results for the reaction of  $\text{CF}^+$  with  $\text{C}_2\text{H}_4$

(Table 1) also fit into the general trend.  $\text{C}_2\text{H}_4$  has no fluorine substituent nor dipole moment, and reaction I is not observed. The analogous outcome of reaction II, producing  $\text{CH}_2\text{F}^+ + \text{C}_2\text{H}_2$ , is the dominant channel. We note, however, that HF elimination is observed in this reaction, but not in those of the fluorinated ethenes.

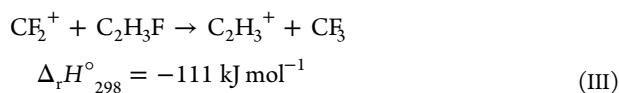
In summary, we suggest that the  $\text{F}^-$ -transfer reactions between  $\text{CF}^+$  and  $\text{C}_2\text{H}_3\text{F}$ ,  $\text{CH}_2\text{CF}_2$ , and  $\text{C}_2\text{HF}_3$  are largely dictated by the dipole moments of these neutral species. The outcome of competition between reactions I and II relates to the magnitude of the dipole moment; the larger  $\mu_D$ , the more preference there is for reaction I to dominate. The different outcomes of reaction II, i.e.,  $\text{F}_2$  vs HF vs  $\text{H}_2$  abstraction, appear to be determined by energetics. They favor  $\text{F}_2$  abstraction, and  $\text{CF}^+$  attacks the molecule preferentially where more fluorine substituents are present.  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{F}_4$  have no dipole moment, and the outcome is the equivalent of reaction II, i.e.,  $\text{H}_2$  and  $\text{F}_2$  abstraction, respectively.

The reactions of  $\text{CF}^+$  with chlorinated ethenes have been performed by Mikhailov et al. using the Birmingham SIFT apparatus.<sup>1,2</sup> The reactions of  $\text{CF}^+$  with  $\text{C}_2\text{H}_x\text{Cl}_{4-x}$  ( $x = 0-3$ ) follow the general trends observed for the fluorinated ethenes. That is, the equivalent of reactions I and II describes all the observed products, with the dominance of reaction I, i.e.,  $\text{Cl}^-$  transfer, decreasing as the number of chlorine atoms increases. The results from the chlorinated ethenes reveal information about reaction II, which is not possible from this fluorinated ethene study. For example, the reaction of  $\text{CF}^+$  with  $\text{C}_2\text{HCl}_3$  produces 23%  $\text{CHCl}_2^+ + \text{C}_2\text{HCl}$ , with the neutral substituted ethyne product containing the fluorine atom. In the analogous reaction with  $\text{C}_2\text{HF}_3$  it might be assumed that the atoms in the neutral product,  $\text{C}_2\text{HF}$ , all originate from the  $\text{C}_2\text{HF}_3$  reactant. The chlorinated ethene study shows that this may not be true, and a more complicated mechanism is probably occurring. The study of the three isomers of dichloroethene also reveals additional information.<sup>1</sup> Most significantly, the reaction of *cis*-1,2-dichloroethene shows no products from the equivalent of reaction I whereas with  $\text{C}_2\text{H}_3\text{Cl}$  and  $\text{CH}_2\text{CCl}_2$  this reaction dominates. This is surprising because of these three chlorinated ethenes it is the *cis*-1,2 isomer that has the largest dipole moment. In fact, of the complete series of chlorinated ethenes reacting with  $\text{CF}^+$ , only  $\text{C}_2\text{H}_3\text{Cl}$  and  $\text{CH}_2\text{CCl}_2$  show products from reaction I; all others only show products from reaction II. It could be significant that these two species are the ones where the chlorine substituents are on the same carbon atom. Yet, if this factor is important in determining if reaction I or II dominates, it is not obvious why reaction II dominates (88%  $\text{CF}_3^+ + \text{C}_2\text{H}_2$ ) with  $\text{CH}_2\text{CF}_2$ , but reaction I dominates (69%  $\text{C}_2\text{H}_2\text{Cl}^+ + \text{CFCl}$ ) with  $\text{CH}_2\text{CCl}_2$ .

**3.2. Reactions with  $\text{CF}_2^+$ .** The RE for  $\text{CF}_2^+$  is 11.36 eV.<sup>18</sup> The results for the reactions of this cation with  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_3\text{F}$ ,  $\text{CH}_2\text{CF}_2$ , and  $\text{C}_2\text{HF}_3$  are presented in Table 1. Because this value exceeds the IE of all four neutral molecules, charge transfer in all reactions is exothermic, and this process does dominate the products. All reactions occur with 100% efficiency. Nondissociative charge transfer is the only channel observed with  $\text{CH}_2\text{CF}_2$  and  $\text{C}_2\text{HF}_3$ . The reaction of  $\text{CF}_2^+$  with  $\text{C}_2\text{H}_3\text{F}$  yields two different ionic products, although the major product still arises from nondissociative charge transfer. The minor product is  $\text{C}_2\text{H}_3^+$ , produced by  $\text{F}^-$  abstraction:



**Figure 1.** Proposed mechanism for (a) the reaction  $\text{CF}_3^+ + \text{C}_2\text{H}_3\text{F} \rightarrow \text{CHF}_2^+ + \text{CH}_2\text{CF}_2$  and (b) the reaction  $\text{CF}_3^+ + \text{CH}_2\text{CF}_2 \rightarrow \text{C}_3\text{HF}_4^+ + \text{HF}$ .



Dissociative charge transfer,  $\text{CF}_2^+ + \text{C}_2\text{H}_3\text{F} \rightarrow (\text{C}_2\text{H}_3\text{F}^+)^* + \text{CF}_2 \rightarrow \text{C}_2\text{H}_3\text{F}^+ + \text{F} + \text{CF}_2$ , is endothermic by 235  $\text{kJ mol}^{-1}$ .

The results from the reaction with  $\text{C}_2\text{H}_4$  are anomalous; charge transfer is observed, but it is the minor channel. In addition, the formation of the major product  $\text{C}_3\text{H}_3\text{F}_2^+$  by H-atom elimination from the adduct is surprising. However, this product has also been observed in the reactions of  $\text{CF}_3^+$  and  $\text{C}_2\text{F}_4^+$  with ethene, and from  $\text{C}_2\text{F}_4^+$  with  $\text{C}_2\text{H}_3\text{F}$  (Tables 1 and 2). The structure of this cation is unknown, but its frequent observation suggests it is relatively stable. Unfortunately, its  $\Delta_f H^\circ$  value is unknown, so  $\Delta_r H^\circ$  values for reactions where it is produced cannot be calculated. Assuming that the  $\text{CF}_2^+ + \text{C}_2\text{H}_4$  reaction is exothermic, we can only determine an upper limit for its enthalpy of formation,  $\Delta_f H^\circ_{298}(\text{C}_3\text{H}_3\text{F}_2^+) < 732 \text{ kJ mol}^{-1}$ , where the stationary electron convention for cations at  $T > 0 \text{ K}$  is used.<sup>27</sup> Its structure is almost certainly  $\text{CF}_2=\text{CH}-\text{CH}_2^+$ .

The adiabatic IE of  $\text{C}_2\text{F}_4$  is 10.11 eV,<sup>15,21</sup> so charge transfer in its reaction with  $\text{CF}_2^+$  is also exothermic. This reaction has been reported by Morris et al.,<sup>9</sup> and unsurprisingly, this reaction proceeds exclusively by charge transfer at the collisional rate.

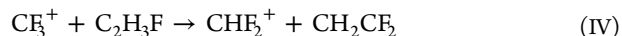
**3.3. Reactions of  $\text{CF}_3^+$ .** The RE for  $\text{CF}_3^+$  is 9.09 eV,<sup>19,20</sup> so as with  $\text{CF}^+$  charge transfer is endothermic for all four reactions. Data for the reactions of  $\text{CF}_3^+$  with  $\text{C}_2\text{H}_x\text{F}_{4-x}$  ( $x = 1-4$ ) are presented in Table 1. Where an association adduct is observed, the He buffer gas pressure is quoted due to its involvement in collisionally stabilizing the energized intermediate formed. We note that this value for the IE of the  $\text{CF}_3$  radical,  $9.090 \pm 0.015 \text{ eV}$ ,<sup>19</sup> is slightly higher than many recent determinations in the range 9.00–9.05 eV, but there is strong evidence that this latest value is the most accurate.

Trends in the reactions of the fluorinated ethenes with  $\text{CF}_3^+$  are apparent.  $\text{F}^-$  abstraction from the neutral appears less favorable as the degree of fluorine substitution increases or the dipole moment decreases; with  $\text{C}_2\text{H}_3\text{F}$  the BR is 75%, with  $\text{CH}_2\text{CF}_2$  only 50%, and with  $\text{C}_2\text{HF}_3$  this reaction is not

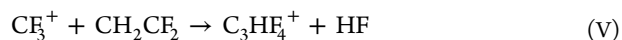
observed. The same trend is apparent in the analogous reaction with  $\text{CF}^+$ ; the smaller the dipole moment of the fluorinated ethene, the less likely  $\text{F}^-$  abstraction appears to occur. Three points should be made regarding  $\text{F}^-$  transfer to  $\text{CF}_3^+$  compared to  $\text{CF}^+$ . First, only the reaction of  $\text{C}_2\text{H}_3\text{F}$  with  $\text{CF}_3^+$  can be compared directly with  $\text{CF}^+$  because the same two product cations are observed. Second, as the BR for  $\text{F}^-$  abstraction decreases, there is no common mechanism in all three reactions taking its place; i.e., there is no significant competition to the  $\text{F}^-$  abstraction reaction. Third, although the value for  $\Delta_f H^\circ_{298}(\text{C}_2\text{HF}_2^+)$  is not known,  $\text{F}^-$  abstraction in the reaction with  $\text{C}_2\text{HF}_3$  is expected to be endothermic; if this is true, using the stationary electron convention  $\Delta_f H^\circ_{298}(\text{C}_2\text{HF}_2^+) > 845 \text{ kJ mol}^{-1}$ .<sup>27</sup> Its structure is almost certainly  $\text{CF}_2=\text{CH}^+$ .

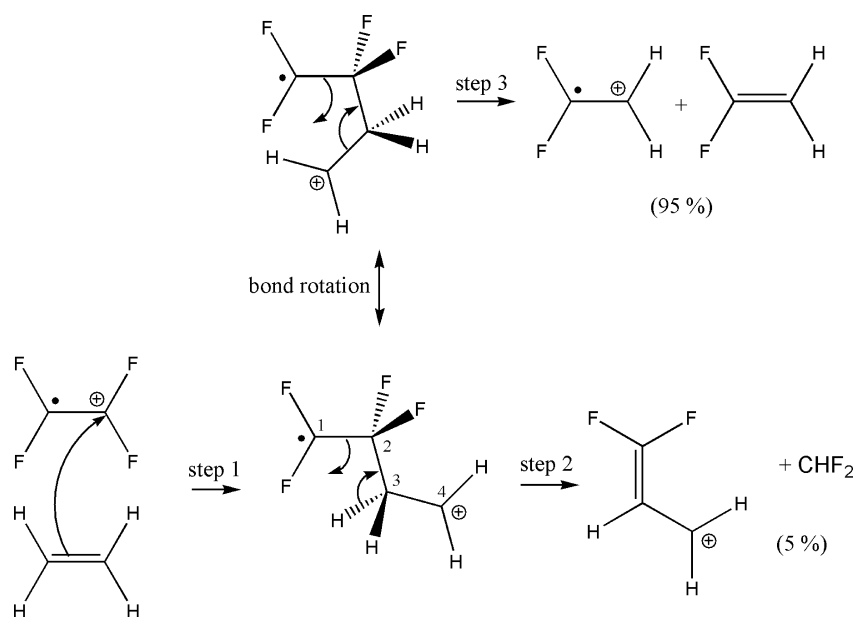
We note the trend in the reaction enthalpies in Table 1, and furthermore, that the reaction  $\text{CF}_3^+ + \text{C}_2\text{F}_4 \rightarrow \text{C}_2\text{F}_3^+ + \text{CF}_4$  is endothermic by 110–120  $\text{kJ mol}^{-1}$ , depending on the value used for  $\Delta_f H^\circ_{298}(\text{C}_2\text{F}_3^+)$ .<sup>20,27</sup> Thus it seems that energetics are more likely to be important in interpreting the results from the  $\text{CF}_3^+$  reactions. Supporting evidence is that, unlike  $\text{CF}^+$ , adduct formation is observed, and the BR increases with increasing fluorine substitution; no adduct is formed in the reaction with  $\text{C}_2\text{H}_3\text{F}$ , the BR for adduct formation is 44% with  $\text{CH}_2\text{CF}_2$ , and with  $\text{C}_2\text{HF}_3$  the BR is 100%. Thus, as  $\text{F}^-$  abstraction becomes energetically less favorable, the lifetime of the reaction complex increases, so it becomes more likely to be collisionally stabilized and observed.

There are also other reactions occurring which do not lead to  $\text{F}^-$  abstraction or adduct formation; for example, the observation of  $\text{CHF}_2^+$  as the minor product (25%) from the reaction of  $\text{CF}_3^+$  with  $\text{C}_2\text{H}_3\text{F}$ :



The proposed neutral product is the 1,1 isomer of difluoroethene because this is the only exothermic outcome. (The cis and trans isomers of 1,2-difluoroethene give reaction enthalpies endothermic by 53 and 57  $\text{kJ mol}^{-1}$ , respectively.<sup>20,27</sup>) Another minority reaction with a BR of 6% which does not fit the general trend is that of  $\text{CF}_3^+$  with  $\text{CH}_2\text{CF}_2$ :





**Figure 2.** Proposed mechanism for the reaction between  $\text{C}_2\text{F}_4^+$  and ethane,  $\text{C}_2\text{H}_6$ .

Reactions IV and V represent thermodynamically favorable exit channels from the adduct that is formed. Proposed mechanisms are presented in Figure 1. We note also that previous work has shown that  $\text{CF}_3^+$  reacts with neutral  $\text{C}_2\text{F}_4$  to produce covalently bonded  $\text{C}_3\text{F}_7^+$ .<sup>9</sup> Finally, in the reaction of  $\text{CF}_3^+$  with  $\text{C}_2\text{H}_4$ ,  $\text{H}^-$  abstraction is observed. This process is not observed in the reactions with the fluorinated ethenes, presumably because it cannot compete with  $\text{F}^-$  abstraction. We recall the comparisons made above between  $\text{F}^-$  abstraction in the reactions of both  $\text{CF}^+$  and  $\text{CF}_3^+$  with the fluorinated ethenes, but the same comment cannot be made regarding  $\text{H}^-$  abstraction in ethene because this outcome in the reaction with  $\text{CF}^+$  is endothermic by  $63 \text{ kJ mol}^{-1}$ . The other product from the reaction of  $\text{CF}_3^+$  with  $\text{C}_2\text{H}_4$  is  $\text{C}_3\text{H}_3\text{F}_2^+$ , produced by  $\text{HF}$  elimination with a BR of 60%.  $\text{HF}$  elimination is also observed from the reaction with  $\text{CH}_2\text{CF}_2$  but as the *minor* product, further demonstrating the dominance of the  $\text{F}^-$  abstraction channel in the fluorinated ethenes and the less dominant  $\text{H}^-$  abstraction reaction from  $\text{C}_2\text{H}_4$ . Tsuji et al. have studied the reaction of  $\text{CF}_3^+$  with ethene in an ion beam,<sup>10</sup> and the results are in satisfactory agreement; the dominant product is  $\text{C}_3\text{H}_3\text{F}_2^+$ , the minor product is  $\text{C}_2\text{H}_3^+$ , and the rate coefficient at 300 K is  $(1.3 \pm 0.3) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . A SIFT study by Morris et al.<sup>8</sup> obtained similar branching ratios but a slower rate of  $0.98 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , closer to our value.

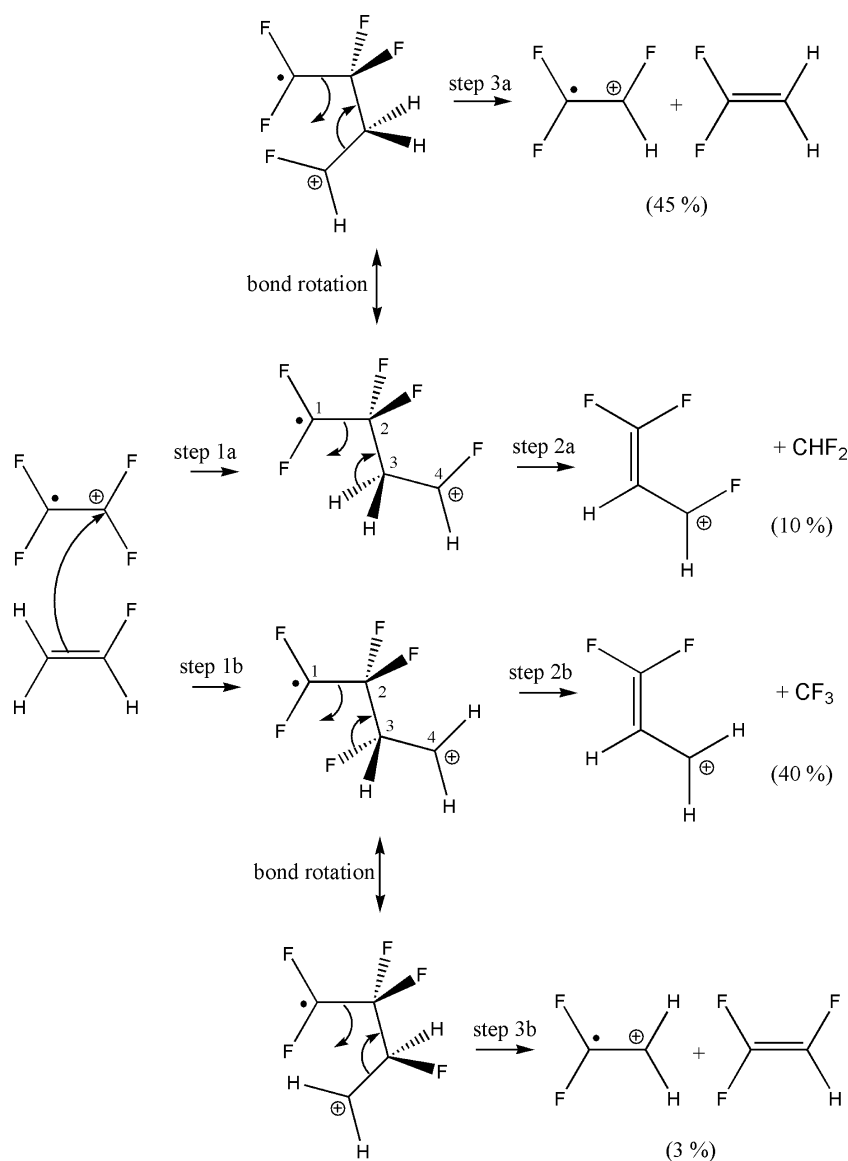
Previous work on chlorinated ethenes report their gas-phase reactions with  $\text{CF}_3^+$ .<sup>1,2</sup> Similarities with the fluoroethenes are noted in the reaction with  $\text{C}_2\text{H}_3\text{Cl}$  and  $\text{CH}_2\text{CCl}_2$ , particularly the former.  $\text{CF}_3^+$  reacts with  $\text{C}_2\text{H}_3\text{Cl}$  to produce  $\text{C}_2\text{H}_3^+ + \text{CF}_3\text{Cl}$  (65%) and  $\text{CHFCl}^+ + \text{C}_2\text{H}_2\text{F}_2$  (35%),<sup>2</sup> very similar to the reaction with  $\text{C}_2\text{H}_3\text{F}$  (Table 1). In both reactions, the  $\text{C}_2\text{H}_2\text{F}_2$  product can only be the 1,1 isomer because the two 1,2 isomers give endothermic reaction enthalpies. The similarities in the reaction of  $\text{CH}_2\text{CF}_2$  and  $\text{CH}_2\text{CCl}_2$  are less striking;  $\text{CF}_3^+ + \text{CH}_2\text{CCl}_2$  exclusively produces  $\text{C}_2\text{H}_2\text{Cl}^+ + \text{CF}_3\text{Cl}$  via  $\text{Cl}^-$  abstraction, whereas the analogous  $\text{F}^-$  abstraction reaction with  $\text{CH}_2\text{CF}_2$  forms only 50% of the observed products (Table 1). Also,  $\text{Cl}^-$  abstraction is observed in the reactions of  $\text{C}_2\text{HCl}_3$  and  $\text{C}_2\text{Cl}_4$ , but the analogous  $\text{F}^-$  abstraction reaction is *not* observed

from  $\text{C}_2\text{HF}_3$  (this work) or  $\text{C}_2\text{F}_4$ .<sup>8</sup> The latter two reactions are expected to be endothermic (see earlier), whereas the former two reactions are clearly exothermic. In fact, new reactions observed in the chlorinated ethenes, which are not equivalently observed in the fluorinated ethenes, appear to arise simply because of the new atom involved, chlorine. For example,  $\text{CF}_3^+ + \text{C}_2\text{HCl}_3$  produces 24%  $\text{CFCl}_2^+ + \text{C}_2\text{HClF}_2$ , whereas this reaction for  $\text{C}_2\text{HF}_3$  is thermoneutral and produces products identical to the reactants. So, although initially it might appear that the differences in the reactions of  $\text{CF}_3^+$  with fluorinated and chlorinated ethenes are significant, they are not and appear to have two dominant explanations. First,  $\text{Cl}^-$  abstraction reactions are energetically more favorable than the equivalent reactions involving  $\text{F}^-$  abstraction. Second, reactions with chlorinated ethenes involve the atoms C, H, F, and Cl, allowing for a larger number of dynamically- and energetically viable exit channels to be available to the reaction complex.

**3.4. Reactions of  $\text{C}_2\text{F}_4^+$ .** The RE for  $\text{C}_2\text{F}_4^+$  is 10.11 eV.<sup>15,21</sup> Like the reactions of  $\text{CF}^+$  and  $\text{CF}_3^+$ , charge transfer with all fluoroethenes is therefore endothermic. Results for the reactions of  $\text{C}_2\text{F}_4^+$  with  $\text{C}_2\text{H}_x\text{F}_{4-x}$  ( $x = 1-4$ ) are given in Table 2. Where an association reaction is observed, as with  $\text{CF}_3^+$  reactions the He buffer gas pressure is quoted. All reactions are relatively slow with  $k_{\text{exp}} < k_0$ , so three-body processes can compete with bimolecular reactions. Many of the ionic products are relatively large, containing three or four carbon atoms. This complicates the data analysis for two reasons. First, it is difficult to suggest confidently an isomeric structure for these product ions. Second, many  $\Delta_f H^\circ_{298}$  values are not known, which prevents  $\Delta_r H^\circ_{298}$  from being calculated for these reactions. Assuming, however, that the reaction is exothermic, it is possible to determine an upper limit for the enthalpy of formation of the product ion (Table 2 and section 4).

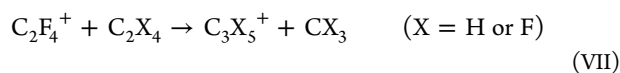
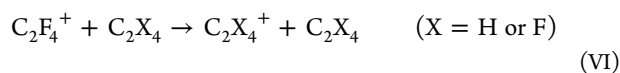
We discuss the structure of the reagent ion,  $\text{C}_2\text{F}_4^+$ . Perfluorination of neutral ethene significantly weakens the  $\text{C}=\text{C}$  bond, the bond strength being ca.  $720 \text{ kJ mol}^{-1}$  in  $\text{C}_2\text{H}_4$  but only  $274 \text{ kJ mol}^{-1}$  in  $\text{C}_2\text{F}_4$ .<sup>20,26</sup> Electron removal from the  $\pi$ -framework weakens the bond even further. Su and Kevan<sup>34</sup>





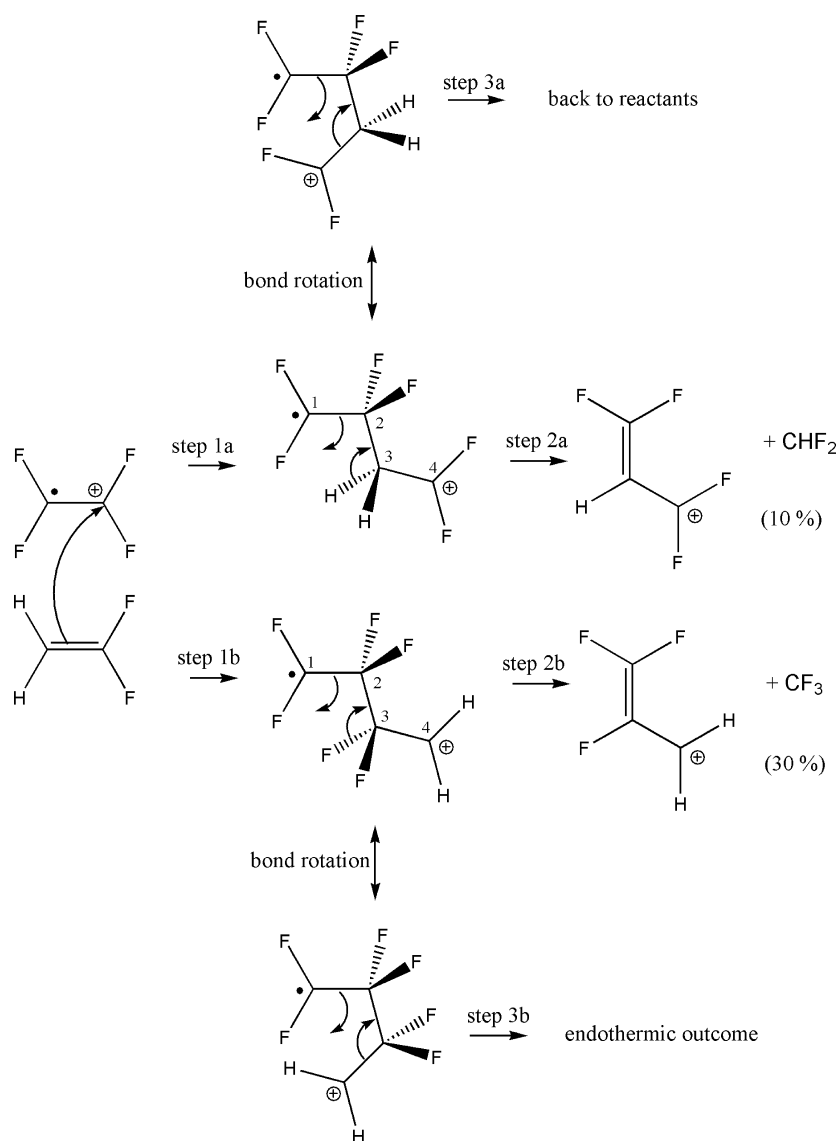
**Figure 3.** Proposed mechanism for the reaction between  $C_2F_4^+$  and monofluoroethene,  $C_2H_3F$ .

have shown that  $C_2F_4^+$  is metastable and will produce  $CF_3^+$  by collision induced dissociation. This involves F-atom migration and cleavage of the carbon–carbon bond. We note also that the first fragment ion formed from dissociative photoionisation of  $C_2F_4$  is  $CF_3^+$ , and not  $C_2F_3^+$  or  $CF_2^+$  from a single bond cleavage.<sup>20,35,36</sup>  $C_2F_4^+$  is therefore represented as  $\cdot CF_2-CF_2^+$  throughout this section. All the products can be divided into three categories. The first is observation of the adduct species. The second is observation of a fluorinated ethene cation which is *different* to the neutral reactant, reaction VI. The third is observation of a cation containing three carbon atoms with the corresponding neutral species being either  $CHF_2$  or  $CF_3$ , reaction VII.



We suggest that products from any of these categories may be explained by one common mechanism, involving formation of a

four-carbon chain adduct that may subsequently fragment either to eliminate  $CX_3$ , reaction VII, or to produce two fluorinated ethenes with one retaining the positive charge. Figure 2 shows this mechanism for the reaction of  $C_2F_4^+$  with  $C_2H_4$ , both the observed product channels (Table 2) being produced from the same four-carbon chain intermediate formed by step 1. This mechanism suggests the product channel  $C_2H_2F_2^+ + C_2H_2F_2$  forms both species as the 1,1 isomer, also the most exothermic outcome. From the BRs, there is an apparent preference for step 3, and not step 2, to follow step 1. The same trend is seen in the reactions of  $C_2F_4^+$  with the fluorinated molecules (Table 2 and discussion below); the channel eliminating  $CHF_2$  is always minor, and the product channels analogous to that in step 3, where possible, have a significant BR. It appears that step 2 in Figure 2 is unfavorable and relatively slow, allowing bond rotation to occur in the intermediate species and step 3 to dominate. Using the upper limit value for  $\Delta_r H_{298}^\circ(C_3H_3F_2^+)$  of  $732 \text{ kJ mol}^{-1}$  determined from the  $CF_2^+ + C_2H_4$  reaction, we determine  $\Delta_r H_{298}^\circ(C_2F_4^+ + C_2H_4 \rightarrow C_3H_3F_2^+ + CHF_2)$  to be  $+127 \text{ kJ mol}^{-1}$ . Even though the BR of this reaction is only 5%, this clearly cannot be

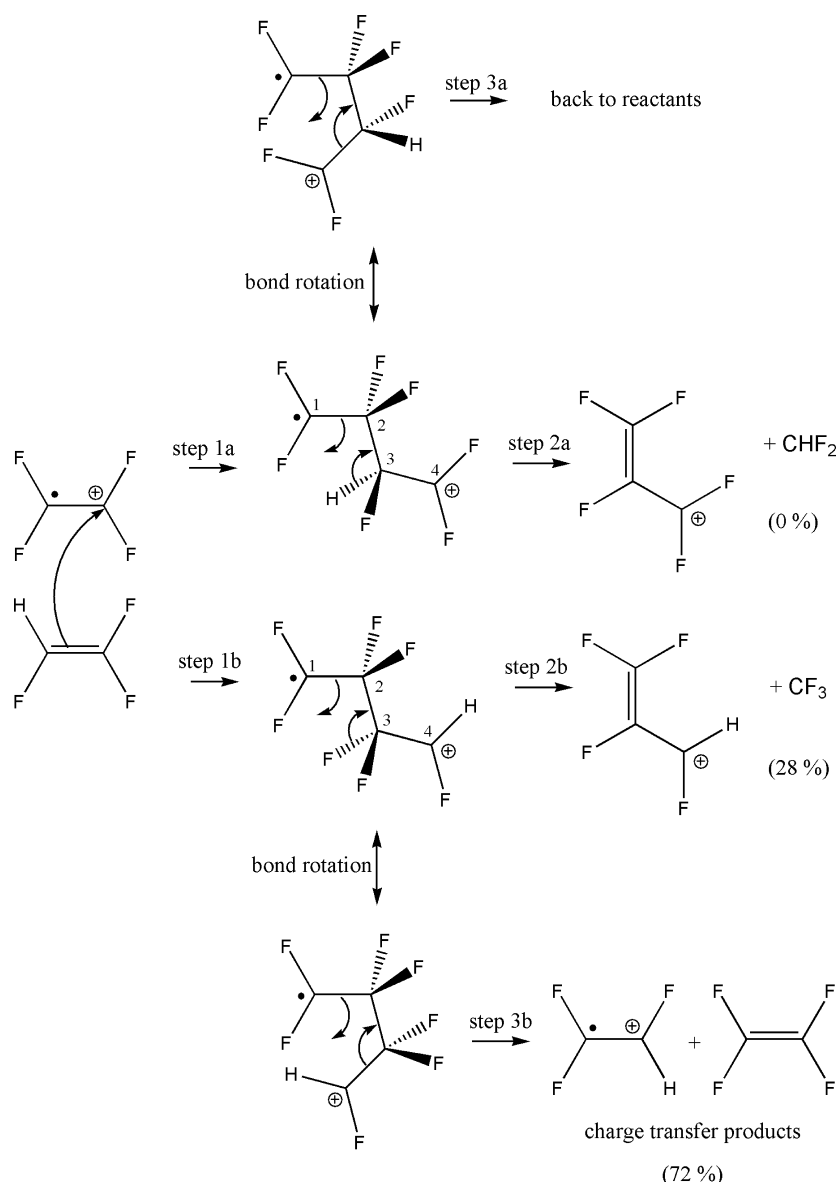


**Figure 4.** Proposed mechanism for the reaction between  $C_2F_4^+$  and 1,1-difluoroethene,  $CH_2CF_2$ .

possible unless  $\Delta_f H^\circ_{298}(C_3H_3F_2^+)$  is significantly less than  $732 \text{ kJ mol}^{-1}$ , i.e.,  $\Delta_f H^\circ_{298}(C_3H_3F_2^+) < 605 \text{ kJ mol}^{-1}$ . The enthalpy change for the dominant channel is exothermic,  $-62 \text{ kJ mol}^{-1}$ , as expected.

Figure 3 shows the proposed mechanism for the reaction between  $C_2F_4^+$  and  $C_2H_3F$ , and all products (Table 2) can be produced by this mechanism. Steps 1a and 1b show that two isomerically different intermediate adducts can form, depending on which carbon in  $C_2H_3F$  forms the bond with a carbon in  $C_2F_4^+$ . Step 1a followed by 2a will produce  $C_3H_2F_3^+$  and  $CHF_2$ , with both substituents on carbon 3 in the adduct being hydrogen. Step 1b, however, produces carbon 3 with one hydrogen and one fluorine substituent in the adduct, so a mixture of  $C_3H_2F_3^+$  (+  $CHF_2$ ) and  $C_3H_3F_2^+$  (+  $CF_3$ ) is produced; note that Figure 3 only shows the latter outcome. From the product BRs there is a preference for elimination of  $CF_3$  over that of  $CHF_2$ . Fluorine is a larger and more polarizable atom than hydrogen, and the C–F bond distance is greater. These facts may explain qualitatively why step 2b preferably eliminates  $CF_3$  rather than  $CHF_2$ , and why step 2b occurs more readily than step 2a. The other products shown in Figure 3 are  $C_2HF_3^+$  and  $CH_2CF_2^+$ , resulting from steps 3a and

3b, respectively.  $C_2HF_3^+$  is the major product (BR = 45%), whereas  $CH_2CF_2^+$  is only a minor product (BR = 3%). A bond rotation is required for either step 3a or 3b to occur, both sterically unfavorable. Therefore, the more favorable step 2b is, the less likely 3b is. The same comment is made with respect to steps 2a and 3a. This may explain why, following step 1a, formation of  $C_2HF_3^+$  by step 3a is the dominant outcome, whereas following step 1b, elimination of  $CF_3$  by step 2b is dominant. An ICR-MS study of the reaction  $C_2F_4^+ + C_2H_3F$  revealed the products  $C_2HF_3^+$  (62%),  $C_3H_3F_2^+$  (31%) and  $C_3H_2F_3^+$  (7%), in good agreement with the dominant products observed in our study. If *only* the mechanism in Figure 3 is considered, then the adduct species, observed as the minor product with BR = 2%, can be produced by either steps 1a or 1b. Given the number of hydrogen and fluorine atoms in the two reactants, the observed adduct may also predominantly be a hydrogen-bonded, rather than a covalent-bonded, species. Because  $C_2F_4^+ + C_2H_3F \rightarrow C_3H_3F_2^+ + CF_3$  has a BR as large as 40%, this reaction is clearly exothermic. We then determine  $\Delta_f H^\circ_{298}(C_3H_3F_2^+) < 628 \text{ kJ mol}^{-1}$ , consistent with the upper limit of  $605 \text{ kJ mol}^{-1}$  derived from the  $C_2F_4^+ + C_2H_4$  reaction.



**Figure 5.** Proposed mechanism for the reaction between  $C_2F_4^+$  and trifluoroethene,  $C_2HF_3$ .

Figure 4 shows how the same mechanism can explain the products observed from the reaction of  $C_2F_4^+$  with  $CH_2CF_2$ . In particular, it shows how elimination of  $CF_3$  and  $CHF_2$  are observed, yet fluorinated ethene cation products from steps 3a or 3b are not; step 3a reverts back to reactants, whereas step 3b is endothermic. Again, a preference to eliminate  $CF_3$  over  $CHF_2$  is observed. The major difference of this reaction compared to that of  $C_2F_4^+$  with  $C_2H_4$ ,  $C_2H_3F$  or  $C_2HF_3$  is the large BR recorded for the adduct species: 60%, compared to 0%, 2%, and 0%, respectively. There is no obvious explanation. In the SIFT study of the reaction of  $C_2F_4^+$  with  $C_2F_4$ , no adduct is observed and the only product is  $C_3F_5^+$  ( $+CF_3$ ).<sup>9</sup> Furthermore, the ICR-MS study of the  $C_2F_4^+$  +  $CH_2F_2$  reaction showed that the only product was  $C_3H_2F_3^+$  ( $+CF_3$ ).<sup>7</sup>

Figure 5 shows the same mechanism for the reaction of  $C_2F_4^+$  with  $C_2HF_3$ . Consistent with the results discussed above, the preference for the intermediate species to eliminate  $CF_3$  rather than  $CHF_2$  is observed, but now the BR for  $CHF_2$  elimination is zero. For this reaction, Anicich and Bowers observed the products  $C_3HF_4^+$  ( $+CF_3$ ) and  $C_3F_5^+$  ( $+CHF_2$ )

with BRs of 92% and 8%, respectively.<sup>7</sup> We observe rather different products:  $C_2HF_3^+$  +  $C_2F_4$  and  $C_3HF_4^+$  +  $CF_3$  with BRs of 72% and 28%, respectively (Table 2). Step 2a shows how  $CHF_2$  elimination is possible, but this step could also lead to  $CF_3$  elimination given that carbon 3 in the intermediate species has both one hydrogen and one fluorine atom attached. We therefore propose that the channel leading to 28%  $CF_3$  elimination is dominated by step 2b.  $C_2HF_3^+$  ( $+C_2F_4$ ) is detected with the largest BR of 72%. Figure 5 shows how this can arise from step 3b, but a simple charge-transfer mechanism could also be occurring. In ion–molecule reactions where charge transfer is observed, it is commonly the dominant product channel, but this reaction is endothermic, albeit by only  $3 \text{ kJ mol}^{-1}$ ; the IE of  $C_2F_4$  is 10.11 eV, that of  $C_2HF_3$  is 10.14 eV.<sup>15</sup> Therefore, the high BR observed for  $C_2HF_3^+$  is not surprising and could result from vibrationally excited  $C_2F_4^+$  in the flow tube, or from the high-energy tail of the thermal distribution of the reactants overcoming the small endothermicity. A charge-transfer reaction normally implies that the two species do not react intimately, but rather an electron from the

neutral molecule hops over to the cation at a significant intermolecular distance.<sup>16</sup> These reactions are usually fast and occur at the collisional rate. Evidence to support the alternative mechanism for  $\text{C}_2\text{HF}_3^+$  production comes from the low value of the reaction efficiency, 17% (Table 2). If the dominant product was formed from fast long-range charge transfer, it is unlikely that the efficiency would be so low. In addition, this efficiency for the reaction of  $\text{C}_2\text{F}_4^+$  with  $\text{C}_2\text{HF}_3$  is much lower than that for  $\text{C}_2\text{F}_4^+$  with  $\text{C}_2\text{H}_4$  (70%),  $\text{C}_2\text{H}_3\text{F}$  (40%) or  $\text{CH}_2\text{CF}_2$  (50%), and none of the products from these three reactions can arise from "fast" processes.

In earlier studies of the ion–molecule reactions of substituted ethene species, it was suggested that a cyclic intermediate, rather than a four-carbon chain, formed which then dissociated to products.<sup>4,7</sup> (Note that in these earlier studies a four-carbon chain intermediate was still needed to explain the  $\text{C}_3\text{X}_5^+$  products ( $\text{X} = \text{H}$  or  $\text{F}$ ) shown in Figures 2–5 by steps 2a and 2b.) The four-carbon chain intermediate is preferred to the cyclic intermediate for two reasons. First, the cycloaddition reaction requires  $\text{C}_2\text{F}_4^+$  to be represented as  $\text{CF}_2=\text{CF}_2^+$ . If the preferred descriptor of  $\bullet\text{CF}_2-\text{CF}_2^+$  is used, it becomes impossible to rationalize the formation of a cycloadduct in step 1. Second, excluding the adduct, the relative BRs of the observed products are best explained by one common mechanism involving one branched, *noncyclic* four-carbon adduct.

#### 4. CONCLUSIONS

The gas-phase reactions of  $\text{CF}^+$ ,  $\text{CF}_2^+$ ,  $\text{CF}_3^+$ , and  $\text{C}_2\text{F}_4^+$  with  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_3\text{F}$ ,  $\text{CH}_2\text{CF}_2$ , and  $\text{C}_2\text{HF}_3$  have been studied using a selected ion flow tube at 298 K. The reactions with  $\text{CF}_2^+$  proceed predominantly by nondissociative charge transfer, whereas those with  $\text{CF}^+$ ,  $\text{CF}_3^+$ , and  $\text{C}_2\text{F}_4^+$  produce products from an adduct complex in which bonds are broken and new ones form.

The dipole moment of the fluorinated ethene is probably a significant factor in the determination of BRs because it is a measure of the nucleophilicity of a fluorine atom in the molecule. This is highlighted by their reactions with  $\text{CF}^+$  and  $\text{CF}_3^+$ . The dynamics involved with  $\text{F}^-$  abstraction are favored when the dipole moment of the fluorinated ethene is large, and the branching into this channel decreases as the dipole moment decreases. However, as branching into  $\text{F}^-$  abstraction decreases, so does the exothermicity of the reaction; in both  $\text{CF}^+$  and  $\text{CF}_3^+$  +  $\text{C}_2\text{HF}_3$  the reaction is expected to be endothermic. It is therefore not easy to separate totally the effects of  $\mu_D$  of the fluorinated ethene from the energetics. It also appears that energetics is the major factor responsible for the apparent preference for  $\text{F}_2$ -abstraction over  $\text{HF}$ -abstraction over  $\text{H}_2$ -abstraction in the reactions of  $\text{CF}^+$  with  $\text{CH}_2\text{F}_2$  and  $\text{C}_2\text{HF}_3$ . The reactions of  $\text{CF}_3^+$  and  $\text{C}_2\text{F}_4^+$  show some similarities. Relative to those of  $\text{CF}^+$  and  $\text{CF}_2^+$ , the rate coefficients and efficiencies in both sets of reactions, are small, ca.  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and sometimes <50%, respectively. Indeed, it is only for reactions of  $\text{CF}_3^+$  and  $\text{C}_2\text{F}_4^+$  where adduct products are observed, but some bimolecular products are also observed from these reactions, for example the neutral product  $\text{CH}_2\text{CF}_2$  from the reactions with  $\text{C}_2\text{H}_3\text{F}$ , and the ionic product  $\text{C}_3\text{HF}_4^+$  from the reactions with  $\text{CH}_2\text{CF}_2$ .

The reactions with  $\text{C}_2\text{F}_4^+$  show many products, but the majority can be explained by a first step that is common to all four of the titled neutral molecules; a four-carbon chain adduct, and not a four-membered ring, is formed. Two pathways then

compete. In one, the intermediate dissociates to yield two fluorinated ethene products (generically described by reaction VI), in the other,  $\text{CF}_3$  or  $\text{CHF}_2$  is eliminated from the intermediate (reaction VII). In reaction VII, a preference for  $\text{CF}_3$  over  $\text{CHF}_2$  elimination is observed.

$\text{C}_3\text{H}_3\text{F}_2^+$  is observed as a product from four of the reactions involving  $\text{CF}_2^+$ ,  $\text{CF}_3^+$ , and  $\text{C}_2\text{F}_4^+$  (Figures 2 and 3). The structure of this cation is almost certainly  $\text{CF}_2=\text{CH}-\text{CH}_2^+$ , and from these four measurements, we determine indirectly  $\Delta_f H_{298}^\circ(\text{C}_3\text{H}_3\text{F}_2^+) < 628 \text{ kJ mol}^{-1}$ , possibly as low as  $605 \text{ kJ mol}^{-1}$  (stationary electron convention).  $\text{C}_3\text{H}_2\text{F}_3^+$  is observed as a product of two reactions involving  $\text{C}_2\text{F}_4^+$ . We determine  $\Delta_f H_{298}^\circ(\text{C}_3\text{H}_2\text{F}_3^+) < 438 \text{ kJ mol}^{-1}$ , possibly as low as  $412 \text{ kJ mol}^{-1}$ . We note that Figure 3 suggests that this ion has structure  $\text{CF}_2=\text{CH}-\text{CHF}^+$  whereas Figure 4 suggests a different isomeric structure of  $\text{CF}_2=\text{CF}-\text{CH}_2^+$ .  $\text{C}_3\text{H}_1\text{F}_4^+$  is produced from three reactions involving  $\text{CF}_3^+$  and  $\text{C}_2\text{F}_4^+$ . Two reactions (Figures 1b and 4) suggest the structure is  $\text{CF}_2=\text{CH}-\text{CF}_2^+$ , one (Figure 5) that it is  $\text{CF}_2=\text{CF}-\text{CHF}^+$ . Three upper limits for  $\Delta_f H_{298}^\circ(\text{C}_3\text{H}_1\text{F}_4^+)$  are determined: 418, 333, and  $202 \text{ kJ mol}^{-1}$ . To our knowledge, there are no other experimental or ab initio values of these enthalpies of formation at 298 K of  $\text{C}_3\text{H}_x\text{F}_{5-x}^+$  ( $x = 1-3$ ) for comparison. The value for  $\text{C}_3\text{H}_5^+$  at 298 K is well established,  $955.4 \pm 2.5 \text{ kJ mol}^{-1}$ ,<sup>37</sup> that for  $\text{C}_3\text{F}_5^+$  only has an approximate upper limit determined of  $84 \pm 20 \text{ kJ mol}^{-1}$ .<sup>38</sup> As expected, the upper limits we have determined for  $\Delta_f H_{298}^\circ(\text{C}_3\text{H}_x\text{F}_{5-x}^+)$  ( $x = 1-3$ ) all fall between these anchor values, and ab initio calculations will be performed in the future. Furthermore, no attempt has yet been made to calculate stationary points of the proposed reaction mechanisms involving  $\text{C}_2\text{F}_4^+$ , i.e., the energetics of the four-carbon intermediates shown in Figures 2–5. Finally, we note that the absence of the  $\text{C}_2\text{HF}_2^+$  product, presumably with structure  $\text{CF}_2=\text{CH}^+$ , from the reaction of  $\text{CF}_3^+$  with  $\text{C}_2\text{HF}_3$  suggests that  $\Delta_f H_{298}^\circ(\text{CF}_2=\text{CH}^+) > 845 \text{ kJ mol}^{-1}$ .

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##### Notes

The authors declare no competing financial interest.

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